How plants eliminate Cu from wastewater

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INTRODUCTION

The high retention capacity of peat can be used to purify wastewaters before their release into the environment. Industrially, this capacity is used in a process called "Jardin Filtrant"™, developed by the Phytorestore company. In this process, wastewaters are filtered through pots, filled with carex (black color, TBR) and sphagnum (brown color, TBL) peat and vegetated with wetland plants, such as *Phragmites australis* (*P.a.*) and *Iris pseudoacorus* (*I.p.*). The aim of this research is to estimate the durability and improve the efficiency of this process, in particular for copper and zinc sorption. To reach this objective, the retention capacity of the vegetated pots and the binding mechanism of the two metal involved on peat and at the peat-root interface must be known.

MATERIALS AND METHODS

Titration experiments and data modeling

The amounts of carboxylic and phenolic groups (T) in the two peats were determined by measuring the acid-base exchange capacity, and simulating the data with the following reactions and constants:

	pK	T mmol/g_{OM}
$>S_i\text{-COOH} \leftrightarrow >S_i\text{-COO}^- + H^+$	4.5	1.0 (TBR) and 0.88 (TBL)
$>S_i\text{-OH} \leftrightarrow >S_i\text{-O}^- + H^+$	8.8	2.8 (TBR) and 1.0 (TBL)

The Cu affinity for the two peats was calculated from isotherm experiments measured at constant pH (pH 4.5 and 5.5) and increasing Cu concentration ($0.5 < Cu_{tot} < 450$ mg/L). Data were modeled with three reactions:

Weak sites	$-S_w\text{-COO}^- + Cu^{2+} \leftrightarrow -S\text{-COO-Cu}^+$	$pK_w = 2.0$
Strong sites	$-S_S\text{-COO-} + Cu^{2+} \leftrightarrow -S_s\text{-COO-Cu}^+$	$pK_{SS} = 4.8$ (TBR) and 5.4 (TBL)
Polymerization sites	$-S_{pol}\text{-COO-} + 2\,Cu^{2+} \leftrightarrow -S_{pol}\text{-COO-}Cu_2^{3+}$	$pK_{pol} = 4.5$ (TBR) and 5.4 (TBL)

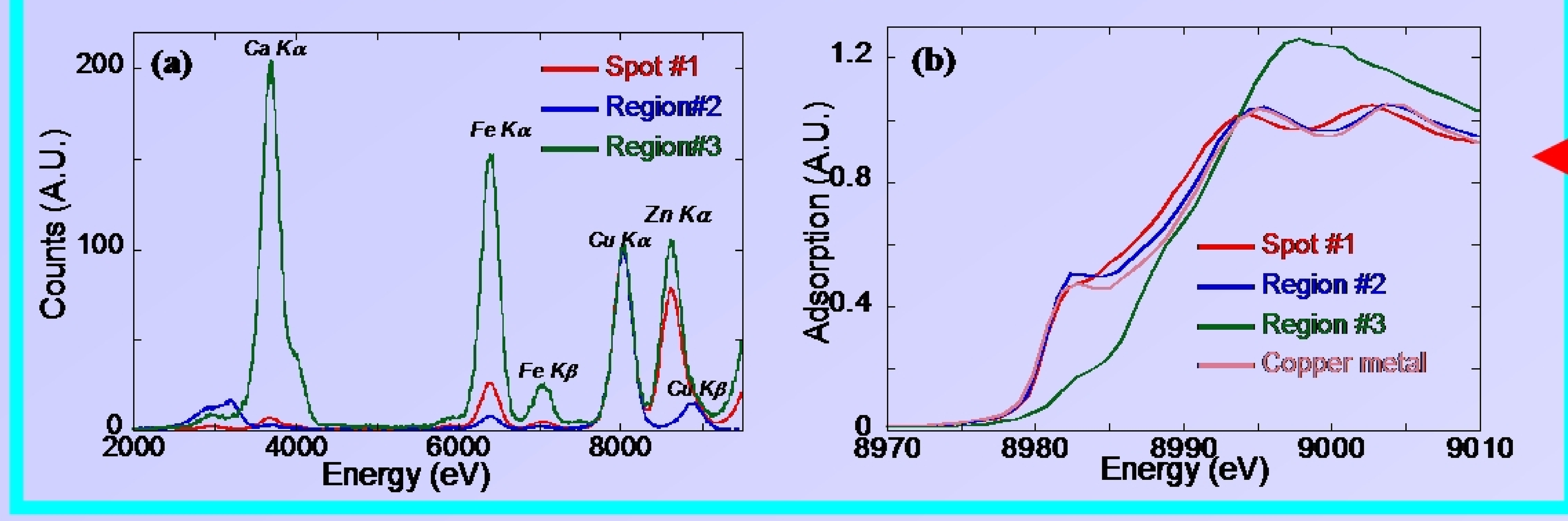
At pH 4.5 and 5.5 Cu binds to carboxylic groups (pK 4.5), not to phenolic groups because their dissociation constant (pK) is too high (8.8).

EXAFS Spectroscopy

The binding mechanism of Cu on peat from sorption isotherm experiments was determined by bulk EXAFS spectroscopy. Spectra were collected on the FAME beamline at the European Synchrotron Radiation Facility (ESRF, France) with a broad X-ray beam (300 * 200 µm), and the data compared with those for Cu-organic complexes of known structure. The distribution of Zn and Cu and their associations with organic matter and major elements in the rhizosphere of *P.a.* from a peat pot used to filtrate lixiviates from a contaminated soil were imaged by micro X-ray fluorescence (µ-XRF). The oxidation state of Cu was determined by micro XANES spectroscopy. Crystalline species were identified by micro X-ray diffraction and EXAFS spectroscopy. This technique also was used to identify non-crystalline species (i.e., Cu complexes). All µ-XRF, µ-EXAFS and µ-XRD data were collected on the 10.3.2-micro-XAS beamline at the Advanced Light Source with a lateral resolution of 5 * 5 µm.

RESULTS

µ-XRF spectra **(a)** and µ-XANES spectra **(b)** from the three spots/regions

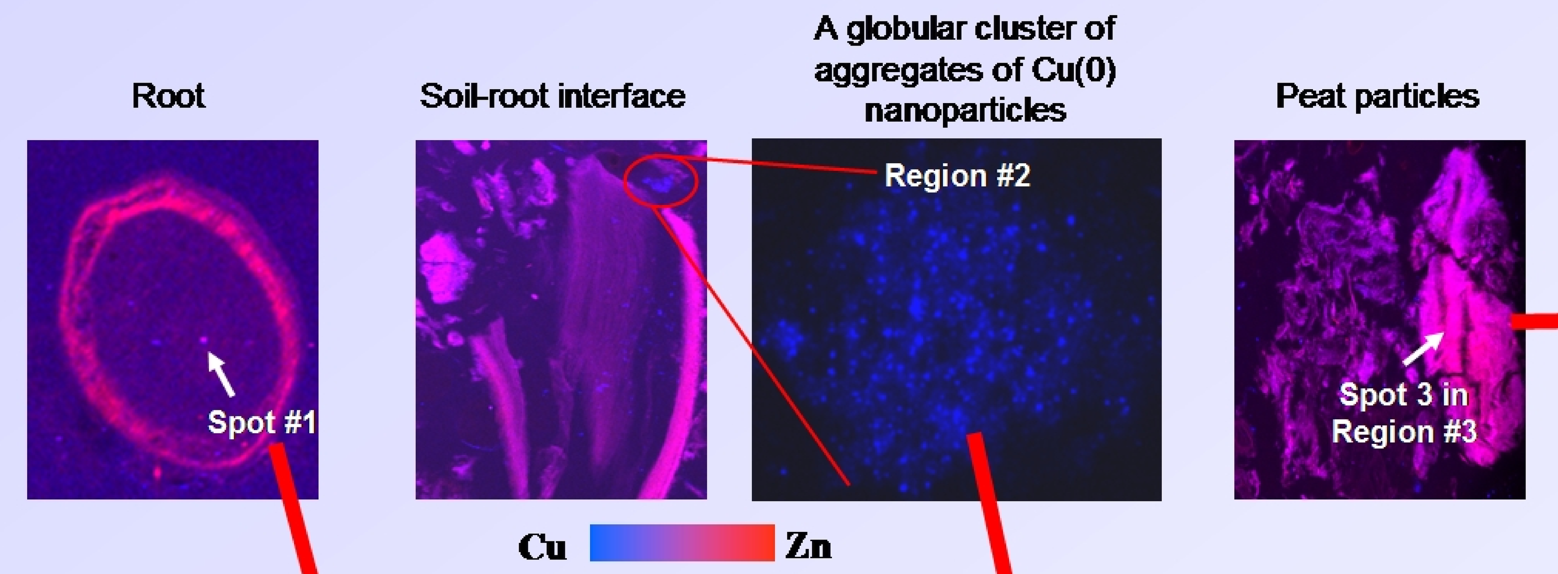


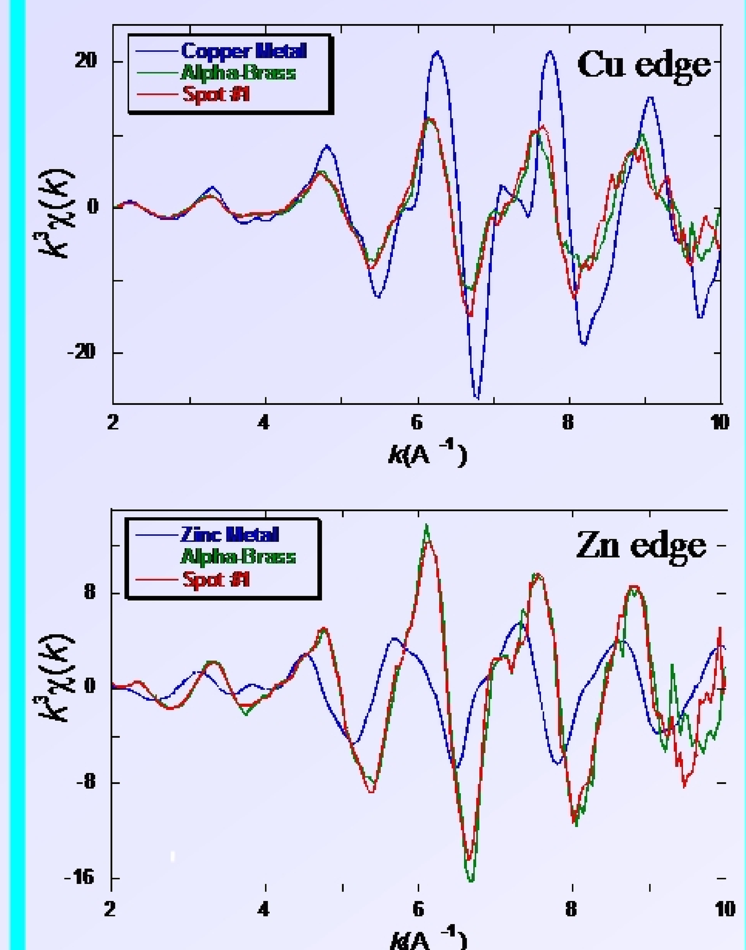
The distribution of Cu and Zn at the soil-root interface of *Phragmites australis* and in peat particles are heterogeneous. Three chemical associations were identified:

Spot #1 : Cu(II) and Zn(II) grain (size=1-5 µm)

Region #2 : Aggregates of Cu(0) nanoparticles (size=1-30 µm)

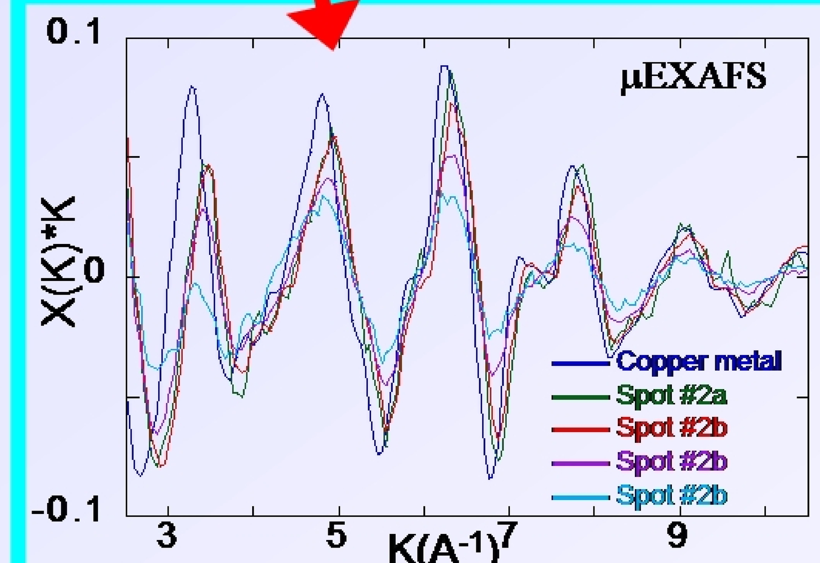
Region #3 : Cu(II) and Zn(II) bound to organic matter. This last form is predominant.



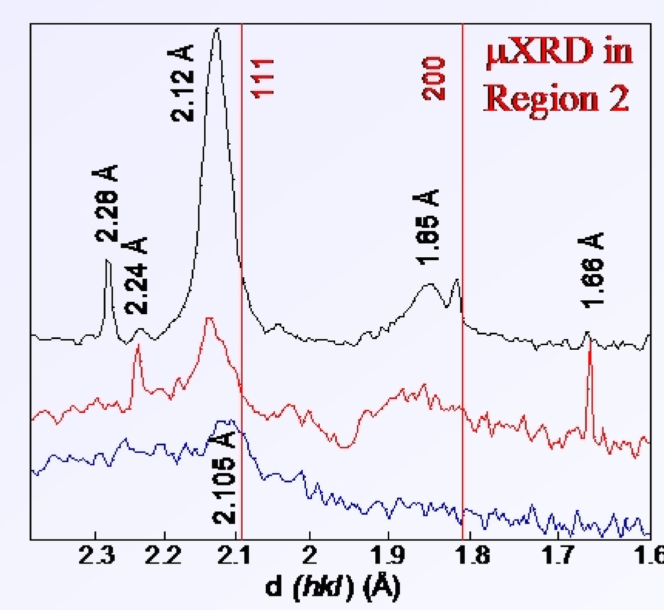


Spot 1 Cu&Zn-edge µEXAFS

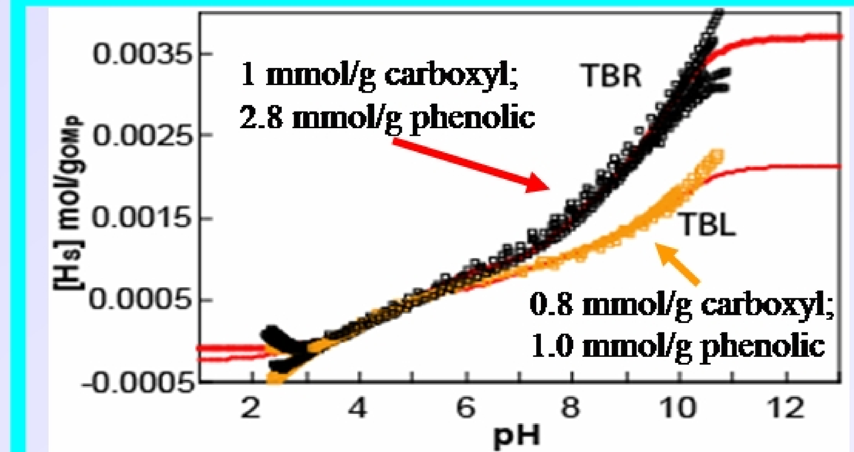
This is an α-brass grain, probably anthropogenic and a minor species.



The spectra from various spots in Region 2 look like those of Cu metal but with reduced amplitude. *These spots contain Cu(0) nanoparticles of various sizes.*

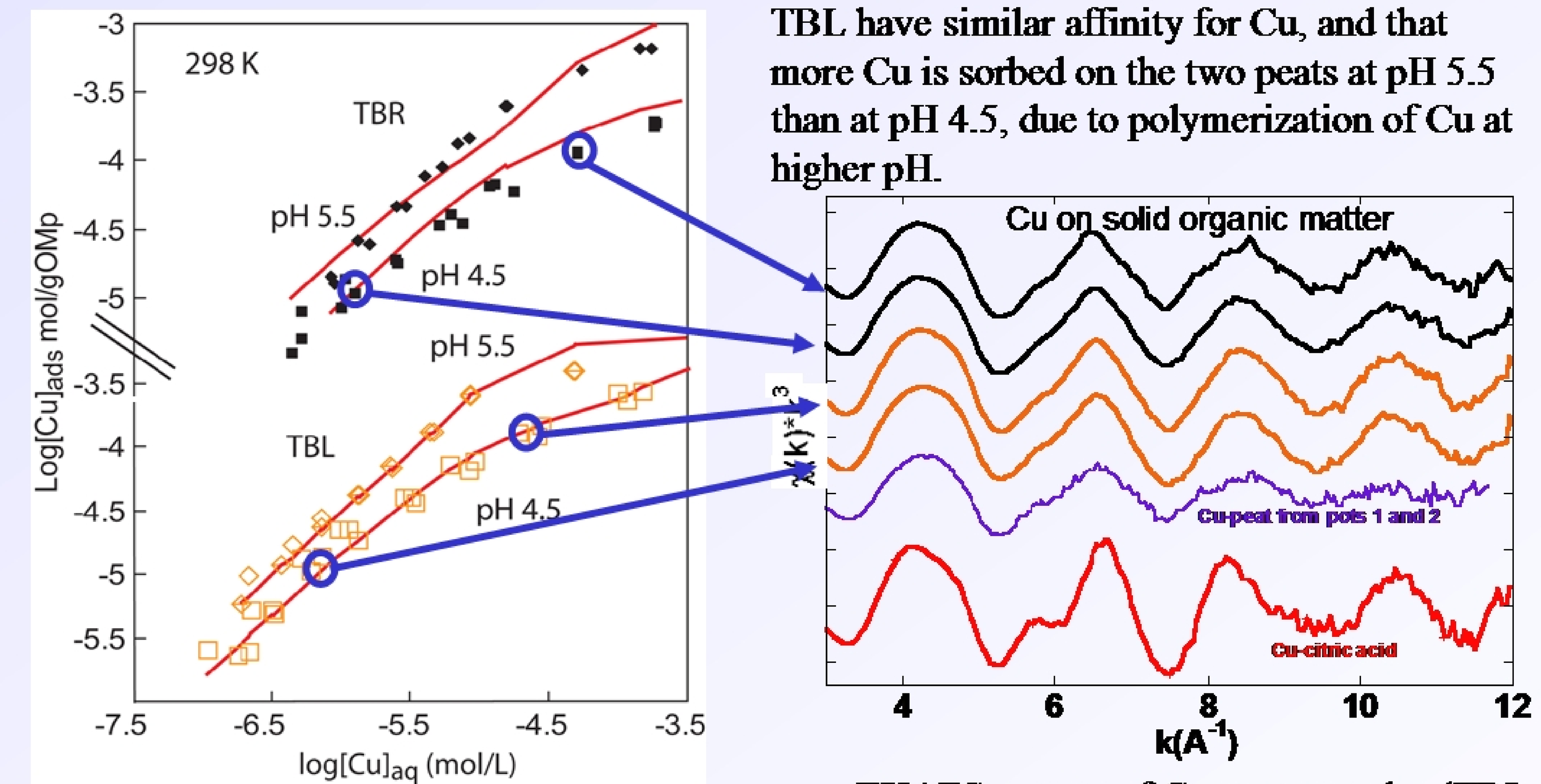


µXRD in Region 2 shows 111 and 200 reflections agreeing with Cu(0), but broadened and slightly shifted w.r.t. bulk (dashed lines).



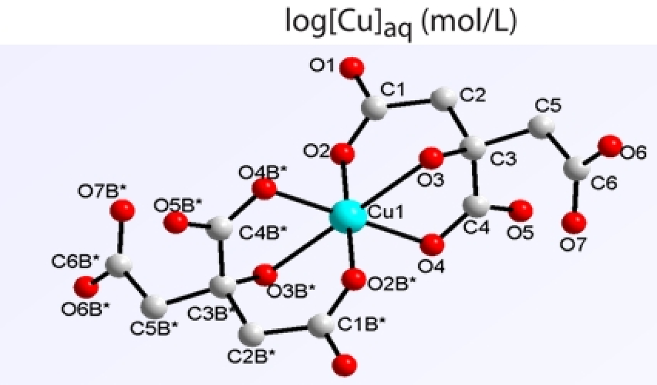
Titration curve (protons released vs. pH) for carex (TBR) and sphagnum (TBL) peats.

TBR has more carboxyl and phenolic groups than TBL, but similar affinity for Cu (see isotherms below).

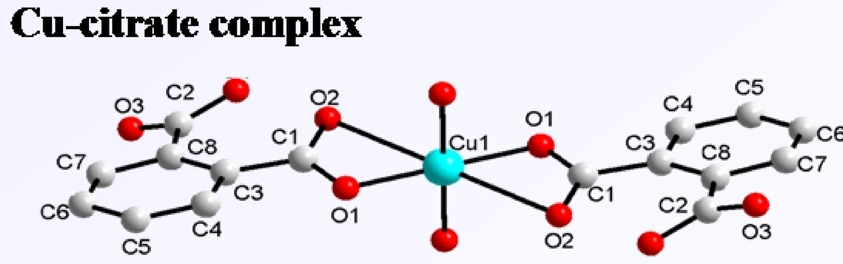


Cu sorption isotherms showing that TBR and TBL have similar affinity for Cu, and that more Cu is sorbed on the two peats at pH 5.5 than at pH 4.5, due to polymerization of Cu at higher pH.

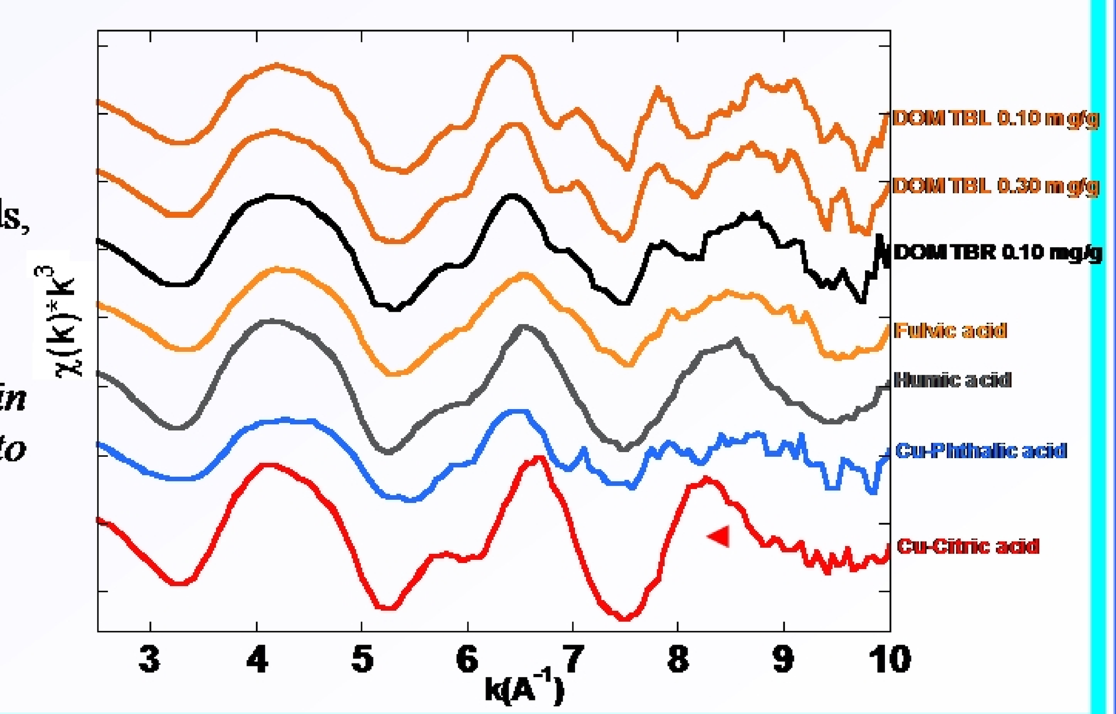
EXAFS spectra of Cu-peat samples (TBL and TBR) from isotherm experiments, and comparison with spectra of natural Cu-peat from a vegetated pot and Cu-citrate reference. The TBL and TBR spectra are similar and independant of the Cu concentration (at least from 0.3 to 2.9 mg Cu/g), and are also similar to the Cu-peat and Cu-citrate spectrum. *Cu has the same citrate-like binding environment in all solid-organic-matter samples.*



Cu-citrate complex



Cu-phthalate complex



Cu EXAFS of dissolved organic matter (DOM) from TBL and TBR peat, fulvic and humic acids, and phthalate and citrate references.

The binding environment of Cu in DOM and fulvic acid is similar to phthalate. In contrast, the Cu complex in humic acid is best described with the citrate reference.

CONCLUSION AND PERPECTIVES

Three Cu-species were identified in the vegetated pot

- **Species 1: α-brass grain probably from anthropogenic activity**
- **Species 2: nanocrystalline Cu(0) particles probably from biological activity**
- **Species 3: Copper complexed to organic matter particles. This natural complex is similar to the complex formed in sorption experiments and resembles Cu-citrate (i.e. chelate ring structure). Copper has a different binding environment when it is complexed in the laboratory to dissolved organic matter from TBR and TBL. This complex is best described as a bidentate chelate, as in phthalate.**

These three species have different binding behavior, which affects the filtering ability of the peat. **The next step of this work is to compare the binding mechanisms of Cu and Zn on peat.**

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